UNIVERSITY OF PENNSYLVANIA

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CLIFTON KERNS

A THESIS

IN CHEMISTRY

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
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THE ELECTROLYTIC REDUCTION OF NITROBENZENE TO AZOXYBENZENE.

By Clifton Kerns.

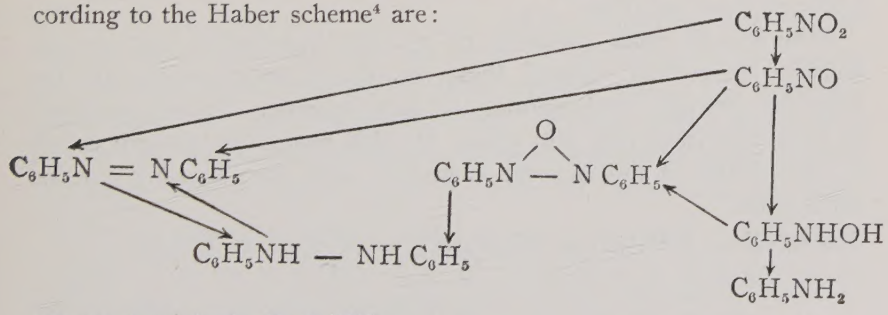
Abstract.

The electrolytic reduction of well stirred aqueous alkaline suspensions of nitrobenzene was studied both in open and in closed cells. Accompanying tabulated results and graphs show the effects of the several variable factors studied on the current efficiency and on the material yield. In general, maximum current and material yields were obtained in closed cell experiments at rather high temperatures (70° - 75° C.) and low current densities (1.5 - 2.5 amp. per sq. dm.).

I. Introduction.

Azoxybenzene, first prepared by Zinin[3] in 1845, is the chief product of the chemical reduction of nitrobenzene in alkaline solution, and of the electrolytic reduction of nitrobenzene in the presence of alkali at normal temperatures using cathode material of platinum, iron, mercury, or nickel.

The primary products in the alkaline reduction of nitrobenzene, according to the Haber scheme[4] are:



[3] Zinin, J. für Chemie, **36**, 98 (1845).

[4] Elbs, "Elektrolytische Darstellung," p. 59, Wm. Knapp, Halle a.S. (1902); Haber, Z. Elektrochem., **4**, 506-513 (1898); Haber and Schmidt, Z. Physikal. Chem., **32**, 271-278 (1900).

Vertical arrows represent electrolytic processes; sloping arrows represent chemical reactions.

The course of the reduction in alkaline solution is as follows:

$$C_6H_5NHOH + C_6H_5NO = C_6H_5N\overset{O}{<}NC_6H_5 + H_2O \quad (1)$$

$$3C_6H_5NHOH = C_6H_5N\overset{O}{<}NC_6H_5 + C_6H_5NH_2 + 2H_2O \quad (2)$$

In the presence of free alkali (1) takes place very quickly. The azoxybenzene may be further reduced to hydrazobenzene which reacts with more of the original nitrobenzene thus:

$$3C_6H_5NH - NHC_6H_5 + 2C_6H_5NO_2 = 3C_6H_5N = NC_6H_5 + C_6H_5N\overset{O}{<}NC_6H_5 + 3H_2O \quad (3)$$

Then, by atmospheric oxygen

$$C_6H_5NH - NHC_6H_5 + O = C_6H_5N = NC_6H_5 + H_2O \quad (4)$$

Löb,[6] however, claims that (3) and (4) are impossible in a cathode chamber in which an alkaline suspension of nitrobenzene is being electrolyzed.

In brief, $C_6H_5NO_2 + 2H = C_6H_5NO + H_2O$ (5)

$$C_6H_5NO + 2H = C_6H_5NHOH \quad (6)$$

$$C_6H_5NHOH + C_6H_5NO = C_6H_5N\overset{O}{<}NC_6H_5 + H_2O \quad (7)$$

Phenylhydroxylamine can not be isolated in the electrolysis of a NaOH solution because of its instability in that medium, but it is readily isolated[7] from the electrolytic reduction of nitrobenzene in an ammoniacal alcoholic solution.

Even though small quantities of phenylhydroxylamine and nitrosobenzene are further reduced, these compounds are converted for the most part, through condensation, into azoxybenzene. Further reduction to hydrazobenzene may also occur, but this compound can not collect in the solution if nitrobenzene is present since the following reaction takes place:

$$3C_6H_5NH - NHC_6H_5 + 2C_6H_5NO_2 = 3C_6H_5N = NC_6H_5 + C_6H_5N\overset{O}{<}NC_6H_5 + 3H_2O \quad (8)$$

[6] Löb, Z. Elektrochem., **7**, 320-338 (1900).

[7] Haber and Schmidt, Z. Physikal. Chem., **32**, 271-278 (1900).

Azoxybenzene does not decompose and is reduced to hydrazobenzene but slowly. In the presence of air, however, the latter is quickly reoxidized to azobenzene. Brockman[8] has given a very thorough treatment of all the reactions, both electrolytic and chemical, which take place in the electrolytic reduction of nitrobenzene both in acid, basic, and neutral environments.

II. HISTORICAL.

Briefly, then, two general methods have been used in the electrolytic reductions of nitrobenzene. In the one, a nitrobenzene solution (usually alcoholic) is electrolyzed; in the other, a suspension of nitrobenzene in some alkaline electrolyte is used.

Using the former method, Elbs[9] in 1893 mentions azoxybenzene as a product of the electrolysis of an alcoholic solution of nitrobenzene using mercury or lead cathode and a 10 per cent KOH solution as catholyte. Haber[10] in 1898 obtained a 76 per cent current yield, using a platinum cathode in an alcoholic alkaline catholyte, and Inoue,[11] in 1921, claimed a 95-100 per cent yield when he substituted nickel for cathode material in an alcoholic NaOH solution. Haber and Schmidt,[12] in 1899, isolated a 21 per cent current yield when they electrolyzed an alcoholic solution of nitrobenzene, using strong ammonia and ammonium chloride for catholyte. Azoxybenzene can be formed even in the presence of acid for Löb,[13] in 1900, reported traces of azoxybenzene from his experiments on the preparation of benzidine, in which experiments he electrolyzed an alcoholic solution of nitrobenzene in the presence of sulfuric acid, using a nickel cathode.

This formation of azoxybenzene in acid solution was confirmed by the fact that Haber[14] found it as a by-product from his preparation of β-phenyl-hydroxylamine, electrolyzing nitrobenzene with a platinum cathode in the presence of acetic acid, and by Flürscheim and Simon[15] who reported numerous cases in which derivatives of azoxybenzene were formed in the presence of strong mineral acids. These investigators stated that both condensation and reduction of the intermediate products of reduction (nitroso and hydroxylamino derivatives) proceed

[8] Brockman, "Electro-Organic Chemistry," pp. 171-252. Wiley & Sons, New York, 1926.
[9] Elbs, Chemiker Zeitung, **17**, 209 (1893).
[10] Haber, Z. Elektrochem., **4**, 506-513 (1898).
[11] Inoue, J. Chem. Ind. Japan, **24**, 121-144 (1921).
[12] Haber and Schmidt, Z. Physikal. Chem., **32**, 271-278 (1900); Z. Elektrochem., **6**, 512 (1899).
[13] Löb, Z. Elektrochem., **7**, 320-338 (1900); Z. Physikal. Chem., **34**, 661 (1900).
[14] Haber, Z. Elektrochem., **5**, 77 (1898).
[15] Flürscheim and Simon, J. Chem. Soc., London, **93**, 1463 (1908).

at a measurable rate whether the solution be acid, neutral, or alkaline. The rate decreases with increase in acid concentration. Darmstädter,[16] in 1907, reported the formation of azoxybenzene in the electrolytic reduction of nitrobenzene dissolved in benzene, using iron or nickel as cathode material in 3 per cent NaOH as catholyte.

Considering now the latter general method of electrolytic reduction, Löb,[17] in 1900, was the first investigator to conceive the idea of electrolyzing a well agitated aqueous suspension of nitrobenzene. Using mercury and nickel cathodes and NaOH as catholyte, he obtained yields of azoxybenzene of 90 per cent or over, when he maintained certain detailed directions as to cell construction and experimental conditions. The fact that no trace of azobenzene could be detected in experiments conducted at temperatures below 90° C. even when a large excess of current was used, caused him to believe that the condensation of phenylhydroxylamine to azobenzene

$$2C_6H_5NHOH = C_6H_5NO + C_6H_5NH_2 + H_2O$$

did not take place in aqueous NaOH suspension as Bamberger[18] and his pupils had found it to do in alcoholic solution of KOH. He claimed also that the action of the oxygen of the air is negligible in the cathode chamber—this in consequence of the high rate of condensation of phenylhydroxylamine and nitrosobenzene to form azoxybenzene, and of the stability of the latter in air. So rapid is this condensation that even the diaphragm between the anolyte and catholyte solutions is superfluous. By using a large cathode and a small anode, Meister Lucius and Brüning[19] claimed satisfactory yields of azoxybenzene by the reduction of nitrobenzene in aqueous alkaline suspension without the use of a diaphragm.

A comprehensive summary of the chemical preparations of azoxybenzene, its reactions, and its constitution has been compiled by Lachmann[20] (1902) while Snowden[21] (1911) has given an excellent detailed review of the literature of its formation both by chemical means and by the electrolytic reduction of nitrobenzene. Brockmann[22] (1926) has given a later and even more detailed account of the historical development of the reduction, and of the different factors which influence it.

[16] Darmstädter, Z. Elektrochem., **13**, 638 (1907).
[17] Löb, Z. Elektrochem., **7**, 300-305 and 320-341 (1900).
[18] Bamberger, Ber. chem. Ges., Berlin, **33**, 271 (1900).
[19] Meister Lucius and Brüning, Z. Elektrochem., **8**, 217 (1902); German patent 127,727.
[20] Lachmann, Am. Chem. J., **24**, 1178 (1902).
[21] Snowden, J. Phys. Chem., **15**, 797-801 (1911).
[22] Brockman, "Electro-Organic Chemistry," pp. 171-252. Wiley & Sons, New York (1926)

III. PURPOSE.

The lack of definite information in all of these investigations as to effects upon yield caused by changes in current density, temperature, stirring, concentration of catholyte solution, ratio of the volume of catholyte solution to nitrobenzene being reduced, and the use of the exact theoretical amount of current rather than the varying excesses used by almost all of the investigators, and the use both of open and closed cells, led to this present study. The hope of the author was to determine some of the unemphasized conditions which must be controlled, in order to produce fairly consistent experimental results and the high material yields claimed.

IV. TYPE OF CELL USED.

The cell used in this investigation (Fig. 1), described by Lukens,[23] consisted of a porous cup of unglazed porcelain, containing a suspension of nitrobenzene in aqueous NaOH and a cylindrical cathode of rolled nickel. Air was excluded from the cell by means of a dome-shaped cylindrical glass cover which was equipped with a mercury seal for the stirrer and two side vents, one for the escape of gas, the other to take the cathode connection. The use of this cover had the advantage of insuring a cell which was air tight and was easy to assemble and to dismantle.

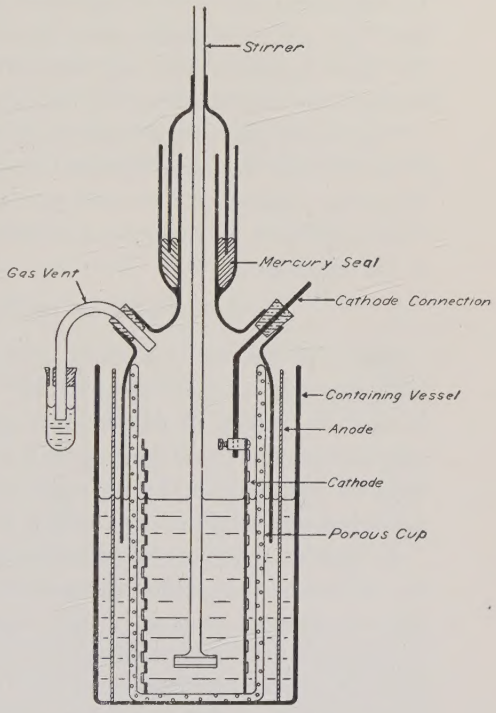


FIG. 1. Cell used in investigation.

In addition, it allowed complete visibility of the inside of the cell. The use of this cell made it possible to keep the current density at the point of maximum rate of hydrogen consumption by so regulating the current that it was just at the point above which hydrogen would escape through the gas vent tube when the delivery end was immersed in water

[23] Lukens, J. Ind. & Eng. Chem., **13**, 562 (1921).

to a depth of about 0.5 cm. This current density, about 1.5 amp. per sq. dm., was used in most of the closed cell experiments in which other variables were studied.

The anode compartment was a two-liter beaker, the anode a cylindrical sheet of iron, and the anolyte a saturated solution of sodium sulfate containing NaOH. Anode material of lead was used instead of iron in a few experiments. Table I presents the results of experiments in which both lead and iron anodes were used. Since both anode materials gave the same material yields and current efficiencies, no distinction is made between the two in compiling the tabulations.

The stirrer was of the centrifugal type used extensively in the laboratories of the Eastman Kodak Company, and in all experiments was rotated at a speed of 900-1,000 revolutions per minute, which speed was found sufficient to maintain a uniform suspension of the nitrobenzene in the electrolyte.

V. DESCRIPTION OF PRELIMINARY EXPERIMENTS.

The experimental procedure used in this investigation was substantially the same as that used by Löb.[24] After the passage of exactly the theoretical amount of current through the well stirred suspension of a weighed amount of nitrobenzene in aqueous NaOH, all unreduced nitrobenzene was removed by the usual steam distillation, and the remaining azoxybenzene solidified by cooling, dried, and then purified.

In spite of rigid control of the factors which were thought to influence the reduction, the results of preliminary experiments were so discordant that any attempt to classify them seemed almost hopeless. The anolyte consisting of a solution of sodium sulfate made slightly acid with sulfuric acid as recommended by Löb[24] was soon found to be unsatisfactory, for after a few experiments the anolyte became stronger in acid content, and the diaphragm no longer allowed a passage of current. The resistance of the cell increased enormously, the temperature increased, and the current fell steadily.

Subsequent examination of one of the porous cups showed that it was clogged by a thin dark red deposit, just halfway the thickness of the diaphragm wall. The deposit, no doubt, was acting as an impermeable membrane, because the substitution of an alkaline anolyte for the acid one eliminated this difficulty. The anolyte used in all later experiments consisted of a saturated solution of sodium sulfate containing sodium hydroxide just in excess of the amount which would be neutralized by

[24] Löb, Z. Elektrochem., **7**, 320-338 (1900).

the acid formed in the anode compartment during the course of the electrolysis.

Cathodes were cleaned before each electrolysis by immersing them momentarily in concentrated nitric acid and rinsing thoroughly with water. The end of each experiment found them still bright and free from deposit.

Slight fluctuations in current were corrected by use of a carbon pile rheostat, placed in series with the regular resistance unit. Constant temperature was maintained by surrounding the cell with a coil through which could be run either steam or cold water. In the low temperature experiments the outer vessel containing the cooling coil was filled with ice, while in the high temperature experiments the outer vessel was heated over a hot plate.

TABLE I.

Comparison of Anode Materials. Closed Cell.

Current density, 2.5 amp./sq. dm. Ampere hours, 16.42. Temp., 25-30° C.

Anode	Electrolyte 2.5 per cent NaOH	$C_6H_5NO_2$ Grams	$C_6H_5NO_2$		Yield of: $(C_6H_5)_2N_2O$			Apparent Current Efficiency*
			Recovered g.	Converted g.	Material		Current Per cent	
					Grams	Per cent		
Iron	300	25	7.80	17.20	10.75	77.8	53.5	68.8
Iron	300	25	7.68	17.32	11.10	79.7	55.3	69.3
Iron	300	25	7.80	17.20	10.62	76.9	52.9	68.8
Lead	300	25	7.68	17.32	11.09	79.6	55.2	69.3
Lead	300	25	7.86	17.14	11.07	80.3	55.1	68.6

* Current efficiency calculated from material consumed.

In a further attempt to get exact experimental checks, two identical cells were set up and electrolyzed in series. A double steam distillation apparatus was also arranged, so that both runs could be steam distilled at the same time. The rate of steam distillation was kept constant in all experiments.

The accuracy with which results can be reproduced may be judged by reference to Table I. This agreement can be expected if all of the precautions just mentioned are carefully observed. The condition of the porous cup itself, however, must have a very definite influence on the yield. Often in experiments in which two cells were being electrolyzed in series, porous cup A would give a yield which was slightly different from that given by porous cup B.

In the following experiment, each of the cups would duplicate its original yield fairly closely, even if the positions of the two cups with

respect to the rest of the cell were interchanged. The experiments tabulated in Table IX illustrate this condition. Note the agreement between the yields from porous cup A in the three experiments, and the agreement between the yields from porous cup B in the same experiments. In an effort to account for this difference, a tabulation was made of the results of many experiments in which cups A and B were electrolyzed in series. This tabulation showed that cup A consistently gave higher yields of azoxybenzene than did cup B, and consistently showed a higher consumption of nitrobenzene.

The NaOH concentration (as determined by titration with acid after the removal of azoxybenzene, etc.) was invariably higher in cup A

TABLE II.

Influence of Temperature. Closed Cell.

Current density, 1.5 amp./sq. dm. Ampere hours, 16.42.

Electrolyte 2.5 per cent NaOH	$C_6H_5NO_2$ Grams	Temp. ° C.	$C_6H_5NO_2$		Yield of: $(C_6H_5)_2N_2O$			Apparent Current Efficiency*
			Recovered g.	Converted g.	Material		Current Per cent	
					Grams	Per cent		
300	25	5-10	10.01	14.99	9.31	77.0	46.3	60.0
300	25	20-25	6.70	18.30	11.70	79.4	58.2	73.3
300	25	35-40	5.06	19.94	13.21	82.4	65.8	79.8
300	25	50-55	3.40	21.60	15.09	86.9	75.1	86.4
300	25	65-70	1.62	23.38	16.60	88.4	82.7	93.5

* Current efficiency calculated from material consumed.

which had given the higher yield, than it was in cup B. The surprising fact was that the cup which gave the higher yield of azoxybenzene, and which contained the more concentrated NaOH solution, was much the less porous of the two cups. This fact would seem to preclude the possibility of the migration of NaOH (excepting, of course, the amount which is formed from the electrolysis of the sodium sulfate) from the anolyte, through the diaphragm, into the catholyte. The low yield given by the more porous cup can be explained, however, on the assumption that the cup absorbs some of the azoxybenzene after it has been formed.

The voltages are not included in the tables because of their relative constancy; slight variations being caused by differences in porosity of the diaphragms, distances between electrodes, etc. The voltages in all experiments varied between 3 and 4.5 volts. In most of the experiments, however, the voltages were between 3 and 3.5 volts.

VI. SEPARATION AND PURIFICATION OF REDUCTION PRODUCTS.

Difficulty was encountered in the separation of unreduced nitrobenzene from the azoxybenzene. The volatility of azoxybenzene in steam made the usual procedure of distilling in steam until nitrobenzene is entirely eliminated, or until only traces of nitrobenzene come over, quite unreliable. Even before all nitrobenzene was expelled, azoxybenzene began to distill over in appreciable quantities. To determine the volatility of azoxybenzene in steam, 20 grams of pure azoxybenzene, recrystallized from alcohol, were placed in a 1 per cent NaOH solution and subjected to steam distillation for 3.75 hours. During this time 6.67 g. distilled over, and 12.34 g. were recovered from the steam distillation flask.

In the actual separation of nitrobenzene from azoxybenzene by steam distillation it was found, however, that by testing small portions of the distillate a fraction was finally obtained which would solidify when collected on ice. Stopping the distillation at this point, while not giving an exact separation of the two compounds, at least afforded means by which a definite reproducible end point could be reached.

Purification of the azoxybenzene was accomplished by placing the crude crystalline material on a small Büchner funnel, applying gentle suction, and melting the crystals with boiling water, whereupon the molten azoxybenzene passed through the filter paper leaving impurities behind. The bottom of the receiving vessel was covered with an ice-water mixture to solidify the product, thus preventing the possibility of any loss due to the use of suction.

The purified product was dried in air and weighed. The material yield was calculated from the weight of the purified azoxybenzene. The impurities, separated by the method just described, consisted of filter paper fibers from the filtration of the crude material, a gray-brown porous cup disintegration product, weighing from 0.1 g. to 0.4 g. for all experiments conducted at ordinary temperatures but going up as high as 10 g. to 20 g. for high temperature experiments, and, in a few experiments, tiny globules of mercury from the mercury seal.

Because of the tediousness and uncertainty of the separation of the nitrobenzene from the nitrobenzene-water mixture, after steam distillation, by using a separatory funnel, extracting with ether, subsequent elimination of ether, and weighing the nitrobenzene, the following method was devised for its rapid and convenient determination. The water-nitrobenzene distillate was caught in an elongated, pear-shaped

vessel terminating in a tube of rather small bore, which was graduated from the bottom up.

The volume of nitrobenzene was read direct, and the weight calculated by multiplying the volume by the density. This was found by weighing a definite volume taken from a sample made up of the combined nitrobenzene distillates from a large number of distillations. This value was almost the same as the density of pure nitrobenzene. The receivers had to be kept clean to prevent nitrobenzene from adhering to the sides.

TABLE III.

Influence of Current Density and Time. Open Cell.

Ampere hours, 16.42. Temperature, 25-30° C.

Electrolyte 2.5 per cent NaOH	$C_6H_5NO_2$ Grams	Current Density amp./dm.^{2}	$C_6H_5NO_2$		Yield of: $(C_6H_5)_2N_2O$			Apparent Current Efficiency*	Time	
			Recovered g.	Converted g.	Material Grams	Material Per cent	Current Per cent		hr.	min
200	25	1.0	10.14	14.86	9.48	79.0	47.1	59.5	6	50
200	25	1.5	7.29	17.71	11.76	82.4	58.5	70.8	4	34
200	25	2.0	11.32	13.68	7.93	70.5	39.5	54.7	3	25
200	25	2.5	12.66	12.34	6.73	67.8	33.5	49.3	2	44
300	25	1.0	6.59	18.41	12.24	82.7	61.0	73.7	4	48
300	25	1.5	7.54	17.46	11.66	83.0	58.2	69.9	3	12
300	25	2.0	9.00	16.00	9.64	74.8	48.0	64.0	2	24
300	25	2.5	11.00	14.00	7.89	70.1	39.2	56.0	1	55
400	25	1.0	5.41	19.59	13.02	82.7	64.9	78.4	3	42
400	25	1.5	6.17	18.83	11.57	76.4	57.8	75.6	2	27
400	25	2.0	8.33	16.67	8.94	66.5	44.5	66.8	1	51
400	25	2.5	11.58	13.42	6.63	61.4	33.0	53.7	1	28

* Current efficiency calculated from material consumed.

Cleaning was accomplished simply by wetting the inside of the container with cleaning solution and rinsing thoroughly with water. The composition of the nitrobenzene distillate will be discussed later.

VII. VARIABLES WHICH INFLUENCE THE REDUCTION.

Temperature. (Table II; Fig. 2.) These results, typical of experiments conducted at low current densities, indicate the gradual increases in nitrobenzene consumed, in azoxybenzene formed, in material yield, in current efficiency, and in apparent current efficiency with increase in temperature. Experiments above 70° C. were not performed, because at temperatures above 90° C. nitrobenzene is reduced to azobenzene[25] rather than to azoxybenzene. Even at 65° to 70° C. the color of the purified azoxybenzene from these experiments differed slightly from the

[25] Löb, Meister Lucius and Brüning, Z. Elektrochem., **10**, 389 (1904).

straw yellow product formed in lower temperature experiments in that it was more orange-yellow. Also, the porous electrolytic cups deteriorated to such an extent owing to the action of 2.5 per cent NaOH at this temperature that they had to be discarded after four or five electrolyses.

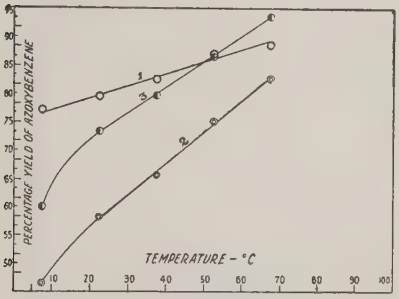


FIG. 2. Temperature. 1, material yield; 2, current efficiency; 3, apparent current efficiency.

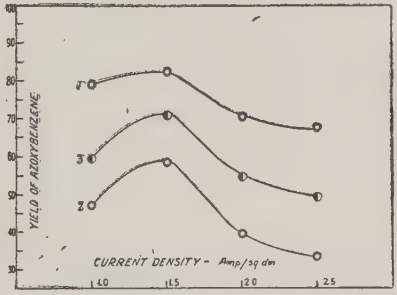


FIG. 3. Current density. (200 cc. electrolyte) 1, material yield; 2, current efficiency; 3, apparent current efficiency.

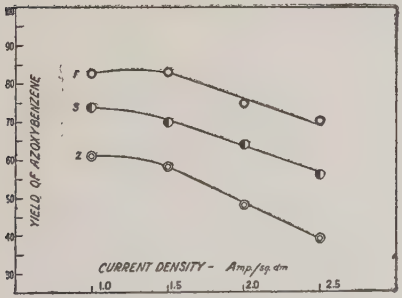


FIG. 4. Current density. (300 cc. electrolyte) 1, material yield; 2, current efficiency; 3, apparent current efficiency.

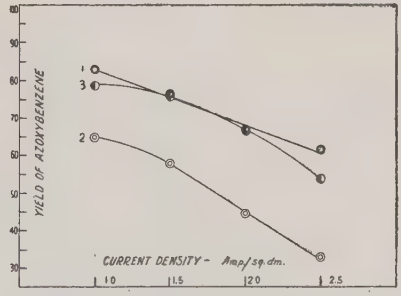


FIG. 5. Current density. (400 cc. electrolyte) 1, material yield; 2, current efficiency; 3, apparent current efficiency.

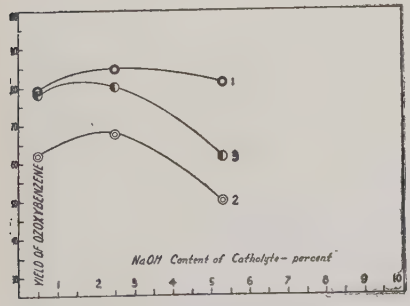


FIG. 6. Concentration of catholyte solution. 1, material yield; 2, current efficiency; 3, apparent current efficiency.

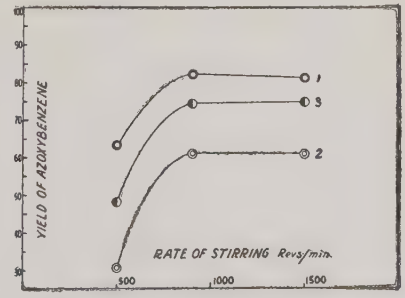


FIG. 7. Stirring. 1, material yield; 2, current efficiency; 3, apparent current efficiency.

The increase in yield with increase in temperature confirmed the anticipated influence of hydrogen overvoltage on the reduction of nitrobenzene. Studies[26] on the influence of hydrogen overvoltage of several cathode materials on the yield of azoxybenzene have shown that metals with a low hydrogen overvoltage give better yields than do metals with a high hydrogen overvoltage. Since hydrogen overvoltage decreases with rise in temperature, then high temperature reductions should give better yields than low temperature reductions. Table II shows this to

TABLE IV.

Influence of Ratio of Catholyte Volume to Nitrobenzene. Open Cell.

Ampere hours, 16.42. Temperature, 25-30° C.

Electrolyte 2.5 per cent NaOH	$C_6H_5NO_2$ Grams	Current Density amp./dm.^{2}	$C_6H_5NO_2$		Yield of: $(C_6H_5)_2N_2O$			Apparent Current Efficiency*
			Recovered g.	Converted g.	Material		Current Per cent	
					Grams	Per cent		
200	25	1.0	10.14	14.86	9.48	79.0	47.0	59.5
300	25	1.0	6.59	18.41	12.24	82.7	61.0	73.7
400	25	1.0	5.41	19.59	13.02	82.7	64.9	78.4
200	25	1.5	7.29	17.70	11.76	85.8	58.5	70.8
300	25	1.5	7.54	17.46	11.66	83.0	58.2	69.9
400	25	1.5	6.17	18.83	11.57	76.4	57.8	75.6
200	25	2.0	11.32	13.68	7.93	70.5	39.5	54.7
300	25	2.0	9.00	16.00	9.64	74.8	48.0	64.0
400	25	2.0	8.33	16.67	8.94	66.5	44.5	66.8
200	25	2.5	12.66	12.34	6.73	67.8	33.5	49.3
300	25	2.5	11.00	14.00	7.89	70.1	39.2	56.0
400	25	2.5	11.58	13.42	6.63	61.4	33.0	53.7

* Current efficiency calculated from material consumed.

be the case. The temperatures recorded in that table are taken from the anolyte solution. Corresponding catholyte temperatures were from four to five degrees higher in every case.

Current Density and Time. (Table III; Fig. 3, 4 and 5.) The effect of cathodic current density was studied using suspensions of nitrobenzene in three different volume ratios of 2.5 per cent NaOH to nitrobenzene in both open and closed cells. Table III summarizes a long series of experiments conducted in open cells. Closed cell experiments will be discussed later. In general, it was found that the nitrobenzene consumed, the material yield, the current efficiency, and the apparent current efficiency all decreased steadily with increase in current density. This is to be expected since increase in current density is accompanied

[26] Löb and Moore, Z. Physikal. Chem., **47**, 418 (1904); Brockman, "Electro-Organic Chemistry," p. 178.

by a corresponding increase in hydrogen overvoltage. It will be noticed, however, that at very low current densities the yields of azoxybenzene, current efficiencies, etc., are not as high as they are at slightly higher current densities, and that after passing an optimum, they decrease steadily with further increase in current density.

Experiments using current densities as low as 1 amp. per sq. dm. with an electrolyte volume of 200 cc. failed to give reproducible results; the reason perhaps being due to the relatively long time required for the complete reduction of the nitrobenzene using this low current density and small catholyte volume. The effect of time on the hydrogen overvoltage might have been sufficient to account for the low yields. Ex-

TABLE V.

Influence of Concentration of Catholyte Solution. Closed Cell.

Current density, 1.5 amp./sq. dm. Ampere hours, 16.42. Temperature, 25-30° C.

Electrolyte NaOH 300 cc.	$C_6H_5NO_2$ Grams	$C_6H_5NO_2$		Yield of: $(C_6H_5)_2N_2O$			Apparent Current Efficiency*
		Recovered g.	Converted g.	Material		Current Per cent	
				Grams	Per cent		
0.5%	25	5.50	19.50	12.42	79.1	61.8	78.0
2.5%	25	5.04	19.96	13.55	84.4	67.5	79.9
5.3%	25	9.66	15.34	9.99	80.9	49.7	61.4

* Current efficiency calculated from material consumed.

periments using larger catholyte volumes (300 to 400 cc.) in which the time required for complete reduction was shorter, keeping current density constant, show this effect to be less and less noticeable.

Ratio of Catholyte Volume to Nitrobenzene. (Table IV.) The ratio of catholyte volume to nitrobenzene has very little effect upon the reduction. The gradual increase in yields, in current efficiencies, etc., with increase in catholyte volume in experiments using very low current densities may be due entirely to the corresponding decrease in time required for the complete reduction of the nitrobenzene. At higher current densities the yields, current efficiencies, etc., show no consistent change with increase in catholyte volume. After a current density of two amp. per sq. dm. has been exceeded, the optimum volume ratio appears to be that of 25 g. of nitrobenzene suspended in 300 cc. of electrolyte.

Concentration of Catholyte Solution. (Table V; Fig. 6.) The results tabulated (Table V) are representative of experiments carried out

using catholyte solutions of three different concentrations: 0.5 per cent, 2.5 per cent and 5.3 per cent. Highest material and current yields were obtained by using as dilute a NaOH solution as would allow a constant flow of current throughout the electrolysis. In experiments using a very dilute NaOH solution, several minutes were required for the concentration of the electrolyte to build up in the cathode chamber (from the electrolysis of sodium sulfate in the anode compartment) before the electrolysis could proceed smoothly.

In experiments using a catholyte solution of higher concentration, the yields were lower, owing probably to solvent action of NaOH on the reduction products. In spite of the deep red color of the NaOH solution remaining from the steam distillation after the removal of azoxybenzene, however, in no case could a weighable amount of material be recovered by neutralizing the NaOH with acid and extracting with ether. A catholyte solution of 2.5 per cent NaOH was found to give optimum yields.

TABLE VI.

Influence of Stirring. Closed Cell.

Current density, 2.0 amp./sq. dm. Ampere hours, 16.42. Temperature, 25-30° C.

Stirring r.p.m.	Electrolyte 2.5 per cent NaOH	$C_6H_5NO_2$ Grams	$C_6H_5NO_2$		Yield of: $(C_6H_5)_2N_2O$			Apparent Current Efficiency*
			Recovered g.	Converted g.	Material		Current Per cent	
					Grams	Per cent		
500	300	25	12.98	12.03	6.13	63.3	30.5	48.1
900	300	25	6.42	18.58	12.25	82.0	61.0	74.3
1500	300	25	6.30	18.71	12.20	81.1	60.8	74.9

* Current efficiency calculated from material consumed.

TABLE VII.

Influence of Completeness of Reduction. Open Cells.

Current density, 2 amp./sq. dm. Temperature, 25-30° C.

Electrolyte 2.5 per cent NaOH	$C_6H_5NO_2$ Grams	Ampere Hours	$C_6H_5NO_2$		Yield of: $(C_6H_5)_2N_2O$			Apparent Current Efficiency*
			Recovered g.	Converted g.	Material		Current Per cent	
					Grams	Per cent		
300	25	5.00	18.90	6.10	3.22	65.7	52.6	80.1
300	25	10.00	14.06	10.94	6.56	74.5	53.5	71.8
300	25	16.42	9.00	16.00	9.64	74.8	48.0	64.0
300	25	20.00	7.58	17.42	10.19	72.8	41.6	57.1

* Current efficiency calculated from material consumed.

Stirring. (Table VI; Fig. 7.) The effect of stirring has been demonstrated in some of Löb's[27] reductions of azobenzene in alcoholic NaOH solution with a mercury cathode. He found that agitation of the electrolyte increased the current yield of azoxybenzene from 49 per cent to practically 100 per cent. Löb came to the conclusion, however, that stirring was important only insofar as it served to prevent troublesome depletion of nitrobenzene on the cathode surface, and to keep it distributed evenly throughout the catholyte.

The results tabulated (Table VI) are characteristic of many experiments in which the rate of stirring was studied. A preliminary experiment showed that regulating the stirrer speed at 900 - 1,000 revolutions per minute gave a uniform suspension of the nitrobenzene throughout the electrolyte. Actual results showed that experiments using stirrer speeds higher than 900 - 1,000 revolutions per minute gave approximately the same yields as did experiments in which the stirrer speed was kept at 900 - 1,000 revolutions per minute, while lower speeds gave poorer yields.

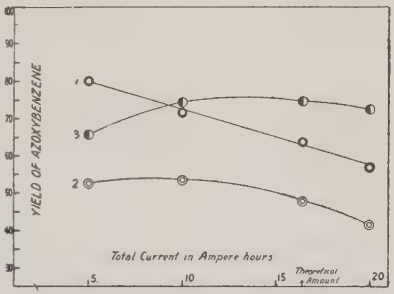


FIG. 8. Effect of total current. 1, material yield; 2, current efficiency; 3, apparent current efficiency.

Completeness of Reduction; Effect of Total Current. (Table VII; Fig. 8.) Table VII shows the effect upon nitrobenzene consumed, material yield, current efficiency, etc., caused by the passage of varying quantities of current through the cell. The use of an excess of current increased the yield, but the increase was much less than the theoretical amount. Material yields were fairly constant, except in experiments in which a small fraction of the theoretical amount of current was used.

In these experiments the material yields were low. Current efficiency was practically constant in all experiments using current below the theoretical amount. Above this amount, current efficiency declined steadily. The gradual fall in apparent current efficiency indicates that the reduction is more energetic in the beginning of the electrolysis when the concentration of nitrobenzene is high than it is later when most of the nitrobenzene has already been reduced. This substantiates the belief that nitrobenzene alone is acting as a cathode depolarizer, and that the

[27] Löb, Z. Elektrochem., 7, 336 (1900).

thicker the layer of nitrobenzene on the cathode surface, the more energetic the reduction.

Comparison of Open and Closed Cells. (Tables VIII, VIIIA, IX and X; Fig. 9 and 10.) As early as 1896 Meldola,[28] studying the chemical reduction of nitrobenzene, suggested that an investigation be carried out to determine the effect upon the completeness of reduction caused by the exclusion of air from the reduction chamber. Löb,[27] studying the electrolytic reduction of nitrobenzene, concluded that in the cathode chamber the action of the oxygen of the air is negligible because of the

TABLE VIII.

Comparison. Open and Closed Cells.

Ampere hours, 16.42. Temperature, 25-30° C.

	Electrolyte	$C_6H_5NO_2$ Grams	Current Density amp./dm.^{2}	$C_6H_5NO_2$		Yield of: $(C_6H_5)_2N_2O$			Apparent Current Efficiency*
				Recovered g.	Converted g.	Material		Current Per cent	
						Grams	Per cent		
	300	25	1.0	4.49	20.51	13.99	84.9	69.6	82.1
	300	25	1.5	5.65	19.35	13.04	83.8	64.9	77.4
	300	25	2.0	6.42	18.58	12.25	82.1	61.0	74.3
Closed	300	25	2.5	7.98	17.02	11.29	82.3	56.2	68.1
Cell	300	25	3.0	11.93	13.07	7.00	66.3	34.8	52.3
	300	25	1.0	6.59	18.41	12.24	82.7	61.0	73.7
	300	25	1.5	7.54	17.46	11.66	83.0	58.2	69.9
Open	300	25	2.0	9.00	16.00	9.64	74.8	48.0	64.0
Cell	300	25	2.5	11.00	14.00	7.89	70.1	39.2	56.0

* Current efficiency calculated from material consumed.

TABLE VIII A.

Comparison. Open and Closed Cells.

Ampere hours, 16.42. Temperature, 25-30° C.

Cell	Electrolyte 2.5 per cent NaOH	$C_6H_5NO_2$ Grams	Current Density amp./dm.^{2}	$C_6H_5NO_2$		Yield of: $(C_6H_5)_2N_2O$			Apparent Current Efficiency*
				Recovered g.	Converted g.	Material		Current Per cent	
						Grams	Per cent		
Closed	300	25	1.0	4.49	20.51	13.99	84.9	69.6	82.1
Open	300	25	1.0	6.59	18.41	12.24	82.7	61.0	73.7
Closed	300	25	1.5	5.65	19.35	13.04	83.8	64.9	77.4
Open	300	25	1.5	7.54	17.46	11.66	83.0	58.2	69.9
Closed	300	25	2.0	6.42	18.58	12.25	82.1	61.0	74.3
Open	300	25	2.0	9.00	16.00	9.64	74.8	48.0	64.0
Closed	300	25	2.5	7.98	17.02	11.29	82.3	56.2	68.1
Open	300	25	2.5	11.00	14.00	7.89	70.1	39.2	56.0

* Current efficiency calculated from material consumed.

[28] Meldola, J. Chem. Soc., London, **69**, T, 13 (1896).

high rate of condensation of the intermediate products of reduction, phenylhydroxylamine and nitrosobenzene, to form azoxybenzene and of the stability of the latter in air.

This conclusion is disproved by the fact that at all current densities studied (Table VIII and VIIIA) the nitrobenzene consumption, azoxybenzene formed, current efficiency, and apparent current efficiency were consistently higher in closed calls than they were in cells which were open to the air. The azoxybenzene from the closed cell experiments was in no wise different from that formed in open cell experiments, and offered no clue as to the cause of the differences in yields or of the possible fate of lost material or of the formation of new substances.

The end products in all experiments consisted of azoxybenzene and unreduced nitrobenzene. In all experiments, however, with the

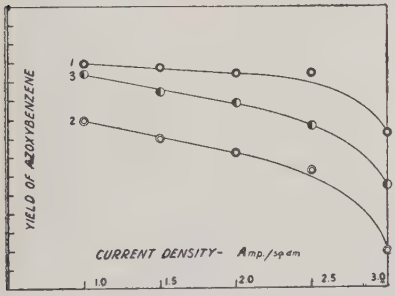


FIG. 9. Closed cell experiments (300 cc. electrolyte) 1, material yield; 2, current efficiency; 3, apparent current efficiency.

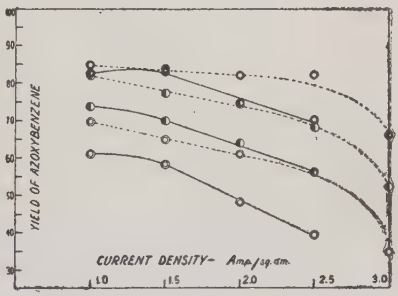


FIG. 10. Comparison of open and closed cell experiments. 1, material yield; 2, current efficiency; 3, apparent current efficiency. Dotted lines represent *closed cell* experiments.

TABLE IX.

Effect of Air After Reduction. Open Cell.

Current density, 2.0 amp./sq. dm. Ampere hours, 16.42. Temperature, 25-30° C.

Exp. No.	Electrolyte 2.5 per cent NaOH	$C_6H_5NO_2$ Grams	$C_6H_5NO_2$ Recovered g.	$C_6H_5NO_2$ Converted g.	Yield of: $(C_6H_5)_2N_2O$ Material Grams	Material Per cent	Current Per cent	Apparent Current Efficiency*	Porous Cup No.	Time between end of reduction and steam distillation
65-A	300	25	8.69	16.31	9.92	75.6	49.3	65.2	7	None.
65-B	300	25	9.45	15.55	9.27	74.2	46.2	62.2	8	None.
64-A	300	25	8.39	16.61	10.12	75.8	50.4	66.5	7	3 hours.
64-B	300	25	9.28	15.72	9.07	71.7	45.2	62.9	8	3 hours.
68-A	300	25	9.04	15.96	9.61	74.9	47.8	63.8	7	Over night.
68-B	300	25	9.28	15.72	9.40	74.4	46.8	62.9	8	Over night.

* Current efficiency calculated from material consumed.

exception of those few in which a measured excess of current was used, the first few drops of nitrobenzene separated by steam distillation were emerald green in color. This color was due, no doubt, to nitrosobenzene,

$$C_6H_5NO_2 + 2H = C_6H_5NO + H_2O$$

This product could not be identified, however, nor could the amount be estimated, for when 200 grams of the combined nitrobenzene distillates were subjected to a second steam distillation no trace of green color was apparent. The most probable fate of the nitrosobenzene is that two molecules of it react with one molecule of azobenzene to form two molecules of azoxybenzene,

$$2C_6H_5NO + C_6H_5N = NC_6H_5 = 2C_6H_5N\begin{matrix}O\\ \diagup\ \diagdown\end{matrix}NC_6H_5$$

or else, by air oxidation,

$$2C_6H_5NO + O_2 = 2C_6H_5NO_2$$

The complete examination of the 200 grams of combined nitrobenzene distillates when subjected to a second steam distillation is presented in Table X. The only indication of the formation of azobenzene in any experiments was that in a few of them the mixture of azoxybenzene and unreduced nitrobenzene as they were removed from the reduction chamber, and each of them after their separation assumed a color that was slightly more orange yellow than their straw yellow color in the other experiments. The NaOH solution from the steam distillation,

TABLE X.

Products Obtained from 200 Grams Nitrobenzene.

200 g. combined nitrobenzene steam distillates when re-steam distilled gave:

174.5 g.	Nitrobenzene (very pale yellow in color).
2.6 g.	Mixture of nitrobenzene and azoxybenzene (red-orange in color and possibly containing traces of azobenzene).
13.7 g.	Azoxybenzene (impure).
190.8 g.	Total.

Fractional distillation of the 174.5 g. of nitrobenzene gave:

1.5 g.	Distillate (slightly below 205° C. corr.).
166.0 g.	Nitrobenzene (B. P. 205°-209° C. corr. representing 95 per cent of this distillate or 83 per cent of the original 200 g. sample).
4.7 g.	Residue (above 209° C. corr. dark red liquid).
172.2 g.	Total.

While from the 13.7 g. of crude azoxybenzene, 11.7 g. of pure material were obtained by crystallization from alcohol. This represented 85 per cent of the weight of the impure azoxybenzene or 6 per cent of the original 200 g. sample.

after the removal of azoxybenzene, changed in color from straw yellow in some cases to a deep wine red color, but in every instance an extraction with ether after acidifying showed that the high coloring was caused by an amount of material too small to be weighed.

Air oxidation must effect the first reduction products of the nitrobenzene rather than the end product, azoxybenzene, which, once formed, seems to be quite stable in air,

$$2C_6H_5NO + O_2 = 2C_6H_5NO_2$$

$$C_6H_5NHOH + O_2 = C_6H_5NO_2 + H_2O$$

This is in agreement with the observations of Bamberger[29] and his students who have shown that phenylhydroxylamine in aqueous alkaline solution is oxidized by air chiefly to azoxybenzene and nitrobenzene, the former resulting from a condensation of the intermediate oxidation product, nitrosobenzene, with phenylhydroxylamine; while the nitrobenzene is an oxidation product of the nitrosobenzene.

The stability of azoxybenzene toward oxidizing agents[30] is substantiated by the fact that experiments (Table IX) in which the mixtures of azoxybenzene and unreduced nitrobenzene direct from the electrolytic cell were allowed to stand for varying lengths of time in vessels open to the air before they were steam distilled, gave the same material yields and current yields as did those experiments in which the mixture was steam distilled immediately following the electrolysis.

VIII. SUMMARY.

1. The efficiency of the reduction of nitrobenzene to azoxybenzene increased with temperature.

2. In general, the yield of azoxybenzene was higher at low current densities than at high current densities.

3. The volume of catholyte had but little effect upon the reduction except in that it determined the time required for complete reduction. An optimum volume ratio for reductions at rather low (1.5 - 2.0 amp. per sq. dm.) current densities was found to be 25 grams of nitrobenzene suspended in 300 cc. of electrolyte.

4. The yields of azoxybenzene were smaller in catholytes of very low electrolyte concentration and in catholytes of very high electrolyte concentration than they were in catholytes of medium concentration. Maxi-

[29] Bamberger, Ber. chem. Ges., Berlin, **33**, 273 (1900).
[30] Löb, Z. Elektrochem., **7**, 337 (1900).

mum yields were obtained by using as low an electrolyte concentration as would allow a steady passage of current throughout the electrolysis. The optimum concentration of electrolyte was found to be 2.5 per cent NaOH.

5. Stirring was important only insofar as it served to keep nitrobenzene distributed evenly throughout the electrolyte. Rates of stirring higher than that required to produce this uniform suspension failed to give higher yields of azoxybenzene.

6. The decrease in the velocity of the reduction with time indicated that nitrobenzene alone was acting as cathode depolarizer. Current in excess of the theoretical amount gave an increase in yield of azoxybenzene, but the increase was much less than the theoretical amount.

7. Closed cell experiments gave higher material yields and higher current efficiencies than did open cell experiments.

ACKNOWLEDGMENT.

This work was undertaken at the suggestion of Professor Hiram S. Lukens and I wish to express my sincere thanks for his help in this investigation.